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| (21) International Application Number: PCT/US97/20830 (22) International Filing Date: 12 November 1997 (12.11.97) (30) Priority Data: 96123343/04 10 December 1996 (10.12.96) RU (71) Applicant (for all designated States except US): SOLUTIA INC. [US/US]; 10300 Olive Boulevard, St. Louis, MO 63141 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MOKRINSKII, Vladimir Vasilievich [RU/RU]; Apartment 94, 13 Russian Street, Novosibirsk, 630058 (RU). SLAVINSKAYA, Elena Markovna [RU/RU]; Apartment 94, 14 Ekvatornaya Street, Novosibirsk, 630058 (RU). NOSKOV, Alexander Stepanovich [RU/RU]; Apartment 14, 9 Tsvetnoy Road, Novosibirsk, 630058 (RU). ZOLOTARSKII, Ilya Aleksandrovich [RU/RU]; Apartment 2, 9 Detskii Road, Novosibirsk, 630058 (RU). (74) Agent: GOODMAN, Kenneth, D.; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210-4433 (US). | | (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: AMMONIA OXIDATION CATALYST COMPRISING ALUMINIUM OXIDE, BISMUTH OXIDE AND MANGANESE OXIDE (57) Abstract <p>Catalyst claimed to be used to produce nitrous oxide by ammonia oxidation with oxygen. The invention aims at providing catalysts exhibiting a high activity, when oxygen content in reaction mixture is close or lower the stoichiometry one, and high selectivity towards nitrous oxide and low selectivity towards nitrogen oxides. The catalyst composition is as follows, mass.‰: manganese oxide (referred to MnO₂) 5.0–35.0; bismuth oxide 4.5–30.0; aluminium oxide 35.0–90.5; specific surface area is 5–80 m²/g.</p> | | |

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AMMONIA OXIDATION CATALYST COMPRISING ALUMINIUM OXIDE, BISMUTH OXIDE AND MANGANESE OXIDE

The present invention describes catalysts to be used for nitrous oxide production by ammonia oxidation with molecular oxygen in chemical industry.

5 Along with a high activity, understood as conversion at a definite residence time, catalysts for ammonia oxidation to produce nitrous oxide should also meet the following demands:

- they should provide a high selectivity towards nitrous oxide and a low selectivity towards nitrogen oxide in the whole temperature range of ammonia oxidation;
- 10 • they should perform well under conditions, when reaction mixture contains oxygen in stoichiometry amount or below the stoichiometry amount.

As a rule, the known catalysts do not comply with all above demands.

Thus a bulk manganese-bismuth catalyst [1] containing 5% Bi_2O_3 and 95% MnO_2 has a low activity. At a temperature of 200°C , when the selectivity towards nitrous oxide is maximum, and equals 88.5% at an inlet ammonia concentration of 10.8 vol.% in the oxygen excess, a complete ammonia conversion occurs at a residence time of 5 s. Meanwhile the selectivity towards NO and NO_2 is 0.9%. As the process temperature increases to 300°C , the yields of nitrous oxide and $\text{NO}+\text{NO}_2$ are 79 and 3.1% respectively. As ammonia concentration decreases to 3.02 vol.%, the selectivity towards nitrous oxide falls to 65%.

20 Therefore, beside a low activity in ammonia oxidation by the oxygen excess, the catalyst shows a high selectivity towards nitrogen oxides.

Another catalyst for ammonia oxidation consists of the oxides of iron, bismuth and manganese in the following ratio: 79.45% Fe_2O_3 , 11.53% Bi_2O_3 , 7.21% MnO_2 [2]. The maximum yield of nitrous oxide in the said catalyst is 82%, and it is attained under the following conditions: temperature - 350°C ; inlet concentrations: ammonia - 10 vol.%, oxygen - 90 vol%. However, at this temperature the selectivity towards nitrogen oxide is 6%. At 300°C the selectivity towards nitrous oxide and nitrogen oxide is 79% and 1.5% respectively. Therefore, the catalyst does not meet all demands in concern, because it has a low selectivity towards nitrous oxide at a high selectivity towards nitrogen oxide.

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Catalyst with a composition of 5% MnO_2 , 5% Bi_2O_3 , 90% Fe_2O_3 [3] is most close in performance and properties to the catalyst claimed in the present invention. It shows the following results. The maximum nitrous oxide yield is 87%, when reaction mixture containing 10% of ammonia in air (thus in oxygen excess, concentration 18.9 vol.%). If
5 reaction mixture contains 1 ammonia part, 5 air parts, and 5 nitrogen parts, and so it is close to stoichiometry (9.1 vol.% ammonia and 9.55 vol.% oxygen), then the yield of nitrous oxide is 81%. At 275-300°C the residence time for complete conversion is 3.6 s. Therefore, the catalyst has a low activity and not high enough selectivity towards nitrous oxide under conditions, when reaction mixture contains ammonia and oxygen in amounts close to
10 stoichiometry.

The present invention aims at providing catalysts that are highly active under conditions, when reaction mixture contains oxygen in amount close or below the stoichiometry one, showing a high selectivity towards nitrous oxide, and a low selectivity towards nitrogen oxide.

15 For the purpose the claimed catalysts for the nitrous oxide production by ammonia oxidation have the following composition (mass.%):

5.0-35.0 - manganese oxide (referred to MnO_2)

4.5-30.0 - bismuth oxide (Bi_2O_3)

90.5-35.0 - aluminum oxide (Al_2O_3).

20 The catalysts of the said composition are prepared by impregnating alumina with a solution of Mn and Bi nitrates, or by mixing the powders of Mn and Bi oxides with the powder of aluminum hydroxide to be then molded, or depositing the said components on an inert support. At the final stage the catalysts are dried, and calcined at 375-550°C. Thus obtained catalysts show a high activity, when the oxygen content in the reaction mixture is
25 close or lower the stoichiometry one, and exhibit a high selectivity towards nitrous oxide, and a low selectivity towards nitrogen oxide.

At a temperature of 350°C, and at a residence time of 0.7 sec, ammonia/oxygen ratio being 1.44, and ammonia concentration being 7.3 vol.%, ammonia conversion on the said catalysts is 82-99.2%. The selectivity towards nitrous and nitrogen oxides is 82-84.6 and 2.1-

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2.7% respectively. After water and ammonia separation the final product contains 79.6-81.7% of nitrous oxide, 4.1-5.25% of nitrogen oxide, and 0.82-0.84% of oxygen.

At a temperature of 300°C, and at a residence time of 1.6 sec, ammonia/oxygen ratio being 1.44, and ammonia concentration being 7.3 vol.%, ammonia conversion on the said catalysts is 82.5-99.0%. The selectivity towards nitrous and nitrogen oxides is 83-86 and 0.3-0.35% respectively. After water and ammonia separation the final product contains 82.2-84.9% of nitrous oxide, 0.6-0.69% of nitrogen oxide, and 0.75-0.77% of oxygen.

The high activity and selectivity of the claimed catalysts in ammonia oxidation to nitrous oxide is provided by its components at the said percent ratios.

Catalyst specific surface area also has a positive effect. The tests show that at a stable high activity the catalyst shows the highest selectivity, when its specific surface area ranges within 5-80 m²/g.

Example 1. Catalyst with a composition of 13%MnO₂/11%Bi₂O₃/76%Al₂O₃ is prepared as follows. 100 g of alumina granules are impregnated by incipient wetness with a solution of Mn and Bi nitrates, are dried in air and then in a drying chamber at 130°C for 2-4 h. Thus obtained product is once again impregnated with a solution of Mn and Bi nitrates, dried in air and in the drying chamber at 130°C for 4 hours. Then the granules were calcined in a furnace at 375-550°C for 2-4 h. Thus obtained catalyst is tested under reaction conditions similar to those described in [3], reaction mixture composition being 9%NH₃ and 9%O₂. At 350°C and at a residence time of 0.7 s ammonia conversion is 99.2%. Selectivity towards nitrous oxide and nitrogen oxide is 87 and 2.8% respectively. At 300°C at the same gas composition and at a contact time of 1.6 s ammonia conversion is 99.4%. Selectivity towards nitrous oxide and nitrogen oxide is 88.6 and 0.30% respectively. Ssp is 10 m²/g.

Example 2. Catalyst prepared as in example 1 is tested at ammonia to oxygen ratio equal to 1.44 and ammonia concentration equal to 7.3 vol.% in the reaction mixture.

At 350°C and at a residence time of 0.7 s ammonia conversion is 82%. Selectivity towards nitrous oxide and nitrogen oxide is 84.6 and 2.7% respectively. In the final product nitrous oxide to oxygen ratio is 97.4, nitrous oxide to nitrogen oxide ratio being 15.6. After

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ammonia and water separation the final product contains 82% of nitrous oxide, 5% of nitrogen oxide, and 0.84% of oxygen.

At 300°C at the same gas composition and at a contact time of 1.6 s ammonia conversion is 82.5%. Selectivity towards nitrous oxide and nitrogen oxide is 86 and 0.35% respectively. In the final product nitrous oxide ratio to oxygen is 110, while nitrous oxide to nitrogen oxide ratio is 121. The final product (after ammonia and water separation) contains 85.2% of nitrous oxide, 0.7% of nitrogen oxide, and 0.78% of oxygen.

Example 3. Catalyst with a composition of 5%MnO₂/5%Bi₂O₃/Fe₂O₃ is prepared as described in [3] and tested under the following conditions: reaction mixture composition - 0.75%NH₃, 1.5%O₂; residence time - 0.072 s, temperature - 350-300°C. At 350°C ammonia conversion is 73%. Selectivity towards nitrous oxide and nitrogen oxide is 76.9 and 3.9% respectively. At 300°C ammonia conversion is 35%. Selectivity towards nitrous oxide and nitrogen oxide is 68 and 1.4% respectively. Ssp is 4 m²/g.

Example 4. Catalyst with a composition of 15%MnO₂/15%Bi₂O₃/70%Al₂O₃ is prepared as in example 1 and tested as in example 2. At 300°C ammonia conversion is 38%. Selectivity towards nitrous oxide and nitrogen oxide is 79 and 1.4% respectively. Ssp is 11 m²/g.

Example 5. Catalyst with a composition of 13%MnO₂/11%Bi₂O₃/76%Al₂O₃ is prepared as in example 1 and tested as in example 2. At 350°C ammonia conversion is 76%. Selectivity towards nitrous oxide and nitrogen oxide is 76% and 3.8% respectively. At 300°C ammonia conversion is 39%. Selectivity towards nitrous oxide and nitrogen oxide is 83 and 1.3% respectively.

Example 6. Catalyst with a composition of 15%MnO₂/7.5%Bi₂O₃/77.5%Al₂O₃ is prepared as in example 1 and tested as in example 2. At 350°C ammonia conversion is 93.2%. Selectivity towards nitrous oxide and nitrogen oxide is 78.7% and 3.9% respectively. At 300°C ammonia conversion is 58.7%. Selectivity towards nitrous oxide and nitrogen oxide is 80 and 1.2% respectively. Ssp is 11 m²/g.

Example 7. Catalyst with a composition of 10%MnO₂/5%Bi₂O₃/85%Al₂O₃ is prepared as in example 1 and tested as in example 2. At 350°C ammonia conversion is 92.5%.

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Selectivity towards nitrous oxide and nitrogen oxide is 80% and 3.7% respectively. At 300°C ammonia conversion is 62.4%. Selectivity towards nitrous oxide and nitrogen oxide is 77 and 1.3% respectively. Ssp is 11 m²/g.

Example 8. Catalyst with a composition of 16%MnO₂/16%Bi₂O₃/68%Al₂O₃ is prepared as in example 1 and tested as in example 2. At 350°C ammonia conversion is 73%. Selectivity towards nitrous oxide and nitrogen oxide is 78.8% and 3.9% respectively. At 300°C ammonia conversion is 37%. Selectivity towards nitrous oxide and nitrogen oxide is 37 and 1.4% respectively. Ssp is 39 m²/g.

Example 9. Catalyst with a composition of 5%MnO₂/4.5%Bi₂O₃/90.5%Al₂O₃ is prepared as follows. 100 g of alumina granules are impregnated by a solution of Mn and Bi nitrates, dried in air and in the drying chamber at 120-130°C for 4 h. The obtained product was calcined in the furnace in air at 375-550°C for 2-4 h. Thus obtained catalyst was tested as in example 2. At 350°C ammonia conversion is 79%. Selectivity towards nitrous oxide and nitrogen oxide is 76% and 3.6% respectively. At 300°C ammonia conversion is 40%. Selectivity towards nitrous oxide and nitrogen oxide is 80 and 1.3% respectively. Ssp is 5 m²/g.

Example 10. Catalyst with a composition of 35%MnO₂/30%Bi₂O₃/35%Al₂O₃ prepared mixing a mass containing 52 g of Mn oxide and Bi oxide powders and 35 g of aluminum hydroxide powder with 25 cm³ of water to obtain a moldable paste. Then the paste was molded as cylinder granules 3 mm in diameter, dried at room temperature for 10 h, dried in the chamber at 120°C for 2 h, and calcined in the furnace at 375-550°C for 2-4 h. Thus obtained catalyst was tested as in example 2. At 350°C ammonia conversion is 77%. Selectivity towards nitrous oxide and nitrogen oxide is 78% and 3.1% respectively. At 300°C ammonia conversion is 39%. Selectivity towards nitrous oxide and nitrogen oxide is 74 and 1.1% respectively. Ssp is 80 m²/g.

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2. Zawadzki, Discussions Faraday Soc., 1950, N8, p.140
3. Schlecht, L., and von Nagel, A., Ger. Patent 503200 (1930)

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Table 1

| example | content, mass. % | | conversion, % | S _{N2O} , % | S _{NO} , % | T°C |
|---------|------------------|--------------------------------|---------------|----------------------|---------------------|-----|
| | MnO ₂ | Bi ₂ O ₃ | | | | |
| 1 | 13 | 11 | 99.2 | 87 | 2.8 | 350 |
| | | | 99.4 | 88.6 | 0.35 | 300 |
| 2 | 13 | 11 | 82 | 84.6 | 2.7 | 350 |
| | | | 82.5 | 86 | 0.35 | 300 |
| 3 | 5 | 5 | 73 | 76.9 | 3.9 | 350 |
| | | | 35 | 68 | 1.4 | 300 |
| 4 | 15 | 15 | 38 | 79 | 1.4 | 300 |
| 5 | 13 | 11 | 76 | 76 | 3.8 | 350 |
| | | | 39 | 83 | 1.3 | 300 |
| 6 | 15 | 7.5 | 93.2 | 78.7 | 3.9 | 350 |
| | | | 58.7 | 80 | 1.2 | 300 |
| 7 | 10 | 5 | 92.5 | 80 | 3.7 | 350 |
| | | | 62.4 | 77 | 1.3 | 300 |
| 8 | 16 | 16 | 73 | 78.8 | 3.9 | 350 |
| | | | 37 | 74.7 | 1.4 | 300 |
| 9 | 5 | 4.5 | 79 | 76 | 3.6 | 350 |
| | | | 40 | 80 | 1.3 | 300 |
| 10 | 35 | 30 | 77 | 78 | 3.1 | 350 |
| | | | 39 | 74 | 1.1 | 300 |

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CLAIMS:

1. A catalyst for production of nitrous oxide, comprising MnO_2 , Bi_2O_3 , and Al_2O_3 .
- 5 2. The catalyst of claim 1, where the catalyst comprises:
about 5.0-35.0 % MnO_2 ;
about 4.5-30.0% Bi_2O_3 ; and
about 35.0-90.5% Al_2O_3 .
- 10 3. The catalyst of claim 1, where the specific surface area of the catalyst is about 5-80 m^2/g .
4. The catalyst of claim 1, where the specific surface area of the catalyst is about 10-40 m^2/g .
- 15 5. The catalyst of claim 1, where the catalyst consists essentially of:
about 5.0-35.0 % MnO_2 ;
about 4.5-30.0% Bi_2O_3 ; and
about 35.0-90.5% Al_2O_3 .
- 20 6. The catalyst of claim 1, where the catalyst comprises:
about 13 % MnO_2 ;
about 11 % Bi_2O_3 ; and
about 76 % Al_2O_3 .
- 25 7. The catalyst of claim 1, where the catalyst comprises:
about 15 % MnO_2 ;
about 15 % Bi_2O_3 ; and
about 70 % Al_2O_3 .

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8. The catalyst of claim 1, where the catalyst comprises:
about 15 % MnO_2 ;
about 7.5 % Bi_2O_3 ; and
about 77.5 % Al_2O_3 .

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9. The catalyst of claim 1, where the catalyst comprises:
about 10 % MnO_2 ;
about 5 % Bi_2O_3 ; and
about 85 % Al_2O_3 .

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10. The catalyst of claim 1, where the catalyst comprises:
about 16 % MnO_2 ;
about 16 % Bi_2O_3 ; and
about 68 % Al_2O_3 .

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11. The catalyst of claim 1, where the catalyst comprises:
about 5 % MnO_2 ;
about 4.5 % Bi_2O_3 ; and
about 90.5 % Al_2O_3 .

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12. The catalyst of claim 1, where the catalyst comprises:
about 35 % MnO_2 ;
about 30 % Bi_2O_3 ; and
about 35 % Al_2O_3 .

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INTERNATIONAL SEARCH REPORT

Inte. onal Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J23/34 C01B21/26 C01B21/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC 6 B01J C01B

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | <p>MASSIMILLA L, JOHNSTONE HF: "Reaction Kinetics in fluidized beds"</p> <p>CHEMICAL ENGINEERING SCIENCE,</p> <p>vol. 16, 1961,</p> <p>pages 115-112, XP002058297</p> <p>See pages 107-108, "Catalyst"</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p> | 1-12 |

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